National Defence Défense nationale

ABSORBANCE CHANGES AS A MEASURE OF [illegible] DEGRADATION

by

J.R. Coleman and L.D. Gallop

DO NOT RETURN
TO DSIS
RETAIN OR DESTROY

DO NOT RETURN
TO DSIS
RETAIN OR DE[illegible]

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 84-[illegible]

[illegible]

[illegible]

National Defence / Défense nationale

ABSORBANCE CHANGES AS A MEASURE OF FUEL DEGRADATION

by

J.R. Coleman and L.D. Gallop
Energy Systems Section
Energy Conversion Division

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 83-33

PCN
25B

December 1983
Ottawa

ABSTRACT

A method for following the course of thermal degradation of aviation turbine fuels was examined, based on the Phillips 5 ml bomb test, and measuring absorbance changes in the thermally stressed fuel at 340 mμ. Comparisons were made with a method based on direct measurement of weights of solid deposited from the fuel.

No correlation was found. The effects of a number of contaminants, and additives frequently employed in jet fuels was surveyed. No consistency was found, and it was concluded that this method offered little promise of being able to rate jet fuels in respect to their thermal stabilities.

RÉSUMÉ

Une méthode pour suivre la dégradation thermique des carburants aviation a été étudiée au moyen de l'essai à la bombe de 5 ml Phillips et de mesures de variations d'absorbance dans le carburant chauffé à 340 mμ. Des comparaisons ont été faites avec une méthode de mesure directe des poids de matières de décontation dans le carburant.

Aucune corrélation n'a été établie. Les effets de certains contaminants et d'additifs souvent utilisés dans les carburéacteurs ont été observés. Aucun résultat systématique n'a été obtenu de sorte qu'il ressort que cette méthode semble peu convenir au classement des carburants aviation en fonction de leur stabilité thermique.

TABLE OF CONTENTS

PAGE

ABSTRACT/RÉSUMÉ iii

TABLE OF CONTENTS iv

LIST OF ILLUSTRATIONS v

LIST OF TABLES vii

1.0 INTRODUCTION 1

2.0 EXPERIMENTAL 3

3.0 RESULTS AND DISCUSSION 4

3.1 General Absorbance-Time Behaviour 4

3.2 Nitrogen Contaminants 5

3.3 Fuel Additives 7

4.0 SUMMARY 11

5.0 REFERENCES 12

LIST OF ILLUSTRATIONS

PAGE

Figure 1 - Absorbance Change in 1062 Fuel as a Function of Time of Heating, at Several Temperatures 13

Figure 2 - As Figure 1, 1091 Fuel 14

Figure 3 - As Figure 1, 1075 Fuel 15

Figure 4 - Arrhenius Plots, Temperature Dependence of Rate of Absorbance Change 16
a) 1062 fuel 16
b) 1091 fuel 16
c) 1075 fuel 16
d) 1062 fuel + 50 ppm nitrogen as pyridine 16

Figure 5 - As Figure 1, 1062 + 50 ppm Nitrogen as Pyridine 17

Figure 6 - Absorbance Change with Time for 1062 Fuel, Alone and with Three Levels Added Pyridine 135°C 18

Figure 7 - As Figure 6, with Three Levels Added Indole 19

Figure 8 - (lower) Breakpoint for 1062 Fuel, Alone and with Three Levels Added Indole 20

(upper) Deposition Effects in Jet A Fuel as a Function of Indole Concentration (from reference (9)) 20

Figure 9 - As Figure 8, with Three Levels Added Pyridine 21

Figure 10 - Effect of Pyridine, 2, 6-Lutidine and Trimethylpyridine on Absorbance Change in Fuel 1062, 135°C 22

Figure 11 - As Figure 10, with Quinoline, 2, 5 Dimethylquinoline and 8-Hydroxyquinoline as Additives 23

Figure 12 - As Figure 10, with Pyrrole, and N-Methylpyrrole as Additives 24

Figure 13 - As Figure 10, with Indole, 2-Methylindole and Carbazole as Additives 25

Figure 14 - Relation Between Effectiveness of Nitrogen Compounds in
a) Promoting Solids Deposition from Heated Fuel (Ref. 9) and 26
b) Development of Absorbance in Heated Fuel 26

PAGE

Figure 15 - Absorbance Change in Fuel 1091, Heated Alone and with EGME (0.2% V/V) 27

Figure 16 - Absorbance Change in Fuel 1091, Heated Alone and with Tolad 245 (45 mg/l) 28

Figure 17 - Absorbance Change in Fuel 1091, Heated Alone and with Antioxidant 733 PDA 50 (25 mg/l) 29

Figure 18 - Effect of Prior Room Temperature Contact with Metallic Copper on Absorbance Change in Fuel 1062, Conditions as Listed on Figure 30

Figure 19 - Absorbance Change in Fuel 1062, Heated Alone and with Four Levels of Soluble Copper as Naphthenate 31

Figure 20 - Breakpoint of Fuel 1062, Alone and with Four Levels Soluble Copper as in Figure 19 32

Figure 21 - Effect of Prior Contact (2.5 days) with Copper on Absorbance Change in Fuel 1091, Heated at 139°C 33

LIST OF TABLES

PAGE

Table 1 - Effect of Additives on Kinetics of Fuel Degradation 4

Table 2 - Effect of Additives on Relative Deposition Rates from Fuel 6

Table 3 - Effect of Fuel System Icing Inhibitor on Absorbance 7

Table 4 - Effect of Tolad 245 on Absorbance 8

Table 5 - Effect of Antioxidant on Absorbance 8

Table 6 - Effects of Metallic Copper on Absorbance Breakpoint of 1062 10

Table 7 - Effects of Metallic Copper on Absorbance Breakpoint of 1091 10

1.0 INTRODUCTION

The purpose of this work is to examine absorbance (optical density) changes as a method of following the degradation of aviation turbine fuels when subjected to thermal stress. Thermal degradation differs in some ways from degradation on storage, a problem arising from slow reactions between unstable fuel components with air, water, and container linings, as affected by diurnal or seasonal climatic changes. In commercial fuels a variety of additives - antioxidants, metal deactivators and corrosion inhibitors - are introduced, primarily to reduce the effects of these long term processes. The present concern is with thermal stability - the resistance of the fuel to relatively brief periods of elevated temperature in the presence of air and of heated metal surfaces, i.e. conditions the fuel encounters on board an aircraft.

Jet fuel stability has been reviewed in a CRC publication [1] that summarized all work on test methods previously reported. Attention was given mainly to the Jet Fuel Thermal Oxidation Tester (JFTOT), its predecessor, the ASTM-CRC coker, and to simulators, larger scale devices that provided a more realistic duplication of aircraft fuel storage and delivery systems.

The most widely used method for thermal stability determination employs the JFTOT, and is the basis of an ASTM test method, D3241 [2]. The air-saturated fuel is passed, under specified conditions, over a heated aluminum tube and through a nickel mesh filter. This subjects the fuel to a regime comparable to that which it undergoes on passing through the fuel supply system to the engine, and assesses fuel deterioration in terms of deposits on the heated tube, and formation of particulates that are caught in the filter. When used in a pass-or-fail test, the JFTOT operating temperature is set normally at 260°C. If the heater tube deposit at the end of the test reaches a level 3 when compared with a set of graded colour standards, or if the pressure buildup across the filter due to trapped deposits reaches 25 mm, the fuel fails. A photometric method to measure tube deposits (the MK 8A TDR)*, supposedly more objective, gives numerical readings related to deposit depth. It has been proposed that a maximum TDR reading of 15 be adopted as an alternative criterion of failure to the code 3 visual rating, but this has not yet been adopted. TDR readings have been used, however, in investigative work, directed to a more quantitative measure of fuel stability [3]. In particular, runs are conducted at a series of temperatures and by interpolation a temperature (the JFTOT break point) determined at which the TDR rating just reaches 15 or some other arbitrary value taken as indicating failure. In this way comparative stabilities can be assigned.

From time to time small scale static tests have been proposed, based on absorbance changes in a fuel contained in a vessel and heat-stressed in the presence of air. The most widely discussed of these has been the Phillips bomb test [4]. In this method, a metal bomb containing 5 ml of the fuel, air-saturated, was inserted in a furnace preheated to a set temperature, and after 20 minutes was removed and quenched. The

---

* Supplied by Alcor, Inc., manufacturers of the JFTOT.

transmittance was measured at a wavelength chosen in the region 340-360 mμ. The test was conducted at a number of temperatures, and by interpolation a breakpoint was found, defined as the temperature at which transmittance had fallen by exactly 10%, or 25%, (in two variants of the the test) below its initial value. The actual fuel temperature during the test was variable, because of finite heat-up time; however, the test was still valid as an empirical measure of comparative fuel stability, all experimental conditions being standardized and held the same from run to run.

Another such test is the Thornton flask test, about which full details have not appeared in the literature [5]. Mention should also be made of the work of Snitserov [6] although the brief account available does not provide much detail.

The rationale for these optical measurements is found in the mechanism proposed for deposit formation and discussed in reference [7]. Briefly, it is held that in the early stages of thermal decomposition particles of colloidal dimension separate as a second phase. These particles or micelles, which are the precursors of harmful deposits, while too small by themselves to cause trouble, are large enough to increase light scattering at short wave lengths. The resulting initial decline in transmittance is taken as an index of the inherent instability of the fuel.

Applicability of the 5 ml bomb test has been questioned, particularly with commercial jet fuels which contain an additive package designed to extend storage life [8]. Another question about the method, which is examined here, is whether absorbance increases at the beginning of the heating period do in fact correlate with the appearance of actual deposits on prolonged heating. In this connection Daniel [9] conducted stability investigations on diesel and Jet A fuel, stored at 120°C for periods up to one week, conditions that led to solid deposits. He examined optical methods among others, but adopted finally a procedure of direct weighing of deposits. He also studied the effects of introducing, at several concentration levels, nitrogen-containing compounds known to be detrimental to stability; and in preparation for mechanistic investigations, the rates and activation energies for degradation of Jet A were determined in the presence and absence of a number of nitrogen contaminants. Thus it appeared that optical and deposition methods could be compared in several respects.

In this note, several experimental variations were employed, a comparison of absorbance-time changes over periods of time up to several hours, and a breakpoint determination after a standard 30 minutes heating, in a procedure closely similar to the Phillips test. In work involving one contaminant (copper) a limited amount of JFTOT testing was conducted. However, the bulk of the comparative work with the JFTOT is to be reported separately.

The work to be described falls into several parts. (a) The general course of absorbance change with time was investigated, using several representative fuels subjected to thermal stress; the rates and activation energies derived from these absorbance-time curves at several temperatures were compared with results derived from deposition rates [9]. (b) In a further comparison with Daniel's work, experiments were conducted with a commercial Jet A-1, alone and doped with a variety of nitrogen-containing

additives, to see whether the effects of these additives on deposition rates, as reported by Daniel, parallel, or show any correlation with the absorbance vs time curves that result from heating. (c) The effects of several constituents of the additive package were surveyed. (d) Finally the effect was examined of copper, a notoriously detrimental material, on optical phenomena in heated fuels.

2.0 Experimental

Round-bottomed test-tubes, about 20 cm long, were blown from 14 mm o.d. borosilicate glass tubing, drawn from fresh stock. These were cleaned rigorously (detergent followed by manyfold rinsing and prolonged soaking in deionized water), and dried. To facilitate later sealing-off, the tubes were necked down to a constriction 2-4 mm in diameter, 12 cm from the closed end. Volume measurements made with a number of these vials showed that a volume of 11.7 ± 0.2 ml measured to the narrowest point of the constriction could be reproducibly obtained. A known volume of fuel (4.73 ± 0.01 ml) was introduced into the vials, which after cooling in dry ice were sealed off with the torch. Liquid-air volume ratios (about 2:3) were thus reproducible to ±2%.

For a series of experiments with a succession of heating times at a single temperature, a set of vials was placed in a wire rack, which was inserted in a preheated mechanical convection oven. Each set of experiments included an unsealed vial containing the same volume of paraffin oil, of negligible volatility at the experimental temperatures. The temperature of the paraffin-containing vial was followed continuously by means of an iron-constantan couple and a Fluke 2190A Digital thermometer. This, it was assumed, would represent the heat-up behaviour and approach to final oven temperature of the sealed vials. To further reduce heatup time the oven was set initially 15°C above the desired final (nominal) temperature. When the thermocouple in the paraffin registered a reading of 10-12°C below the desired final temperature, the set point of the oven was cut back, and the paraffin temperature then monitored for the duration of the run and taken as the experimental temperature. With practice conditions were found such that the paraffin oil rose to within 0.5°C of its final equilibrium temperature within 9-10 minutes of inserting the rack in the oven. The resulting inaccuracy becomes less significant, the longer the heating time.

In breakpoint determination, where only a comparison in absorbance increase is wanted between samples heated for 30 minutes in the same batch, the error is self-compensating.

On removal from the oven, samples were quenched in cold water, opened, and the absorbance read at 340 mμ, using a Bausch and Lomb Spectronic 21 spectrometer and cuvettes of 1 cm path length. Spectroscopic grade hexane was used as reference. Results are expressed in absorbance units, referred as convenient for plotting either to hexane or to the initial (unheated) fuel. The breakpoints reported here were determined using an absorbance increase of 0.050 or 0.100. This is the same range as the Phillips test; the 10% and 25% fall in transmittance called for in that test correspond to absorbance increases of 0.045 and 0.125.

Three base fuels were used:

1062 - a commercial Jet A-1 containing the standard additives.
1091 - a Jet A-1 with no additives, provided by the courtesy of Imperial Oil.
1075 - A Jet B, procured in connection with another program, and of interest because of its questionable stability; the JFTOT breakpoint is in the region 250-260°C, which means that it is marginal with respect to the specification test. Most commercial samples pass by a comfortable margin, 20-40°C.

Additives were of reagent grade, and were used as received.

3.0 RESULTS AND DISCUSSION

3.1 General Absorbance-Time Behaviour

The general course of absorbance change was first investigated, using the three fuels above, Jet A-1 with and without additives, and Jet B. Figures 1-3 show representative absorbance-time curves for these three, determined over the first few hours of heating. All displayed approximately linear portions, which were used for rate calculations; though 1062 in particular was irregular, with a marked induction period, shorter as the temperature increased, followed by a linear rise.

Activation energies were calculated from the rate data, as in Figs. 4(a) - 4(c). As mentioned above, only representative absorbance-time curves are shown in Figs. 1-3, which would be overcrowded by inclusion of all the runs used to derive the activation energies.

These results were compared with the kinetic data reported by Daniel [9], who investigated the thermal decomposition of Jet A alone and after addition of four nitrogen-containing contaminants. From his report it is possible to estimate both relative rates and activation energies, rates being taken in all cases as proportional to accumulated deposit weight after 168 h:

TABLE 1

EFFECT OF ADDITIVES ON KINETICS OF FUEL DEGRADATION

	JET A	JET A PLUS PYRIDINE	JET A PLUS QUINOLINE	JET A PLUS PYRROLE	JET A PLUS INDOLE
Rate at 120°C $g/mm^2 \times 10^7$	8	22	24	12	17
E(cal)	10	33	32	21	28

All the contaminants affected the mechanism of decomposition as shown by the increase in temperature dependence of solid deposition; rates of deposition at one temperature (120°C) invariably increased also.

While Daniel found deposition rates were increased by pyridine addition, as shown by accumulated deposit after 168h, absorbance buildup was retarded after the initial acceleration (cf curves in Figs. 1 and 5 at the same temperature). Qualitatively similar results were obtained using 1062 with a variety of nitrogen-containing additives (see below). From the variation in activation energies seen in Fig. 4, it is apparent that, at least as reflected by absorbance changes, no common mechanism exists for decomposition of fuels; also, comparing activation energies for original and pyridine-treated 1062 (31 and 27 KCal) with Daniel's results in Table 1, processes leading to absorbance change during the first few hours show a quite different time and temperature dependence from those responsible for material deposit after prolonged stand.

3.2 Nitrogen Contaminants

Daniel [9] investigated also the effect of contaminant concentration with Jet A, and found that with two compounds, pyridine and quinoline, the deposition rate was strongly dependent on concentration, whereas with indole and pyrrole the rate was nearly insensitive to additive level. Absorbance-time determinations made under closely comparable conditions, employing three levels of pyridine and indole, are shown in Figs. 6 and 7. Some resemblances to Daniel's results are seen, particularly in the early stages of absorbance buildup. Absorbance-time curves for the control and for indole-containing samples are nearly coincidental, while pyridine accelerates the initial absorbance development. On the other hand, with neither additive is there any dependence on the additive level, and after about 4.5 h the absorbance of the control overtook that of the pyridine-spiked samples.

Breakpoint determinations were carried out on these fuels, in the modification of the Phillips procedure already mentioned. Duplicate samples of fuels, with and without additives were incubated 30 minutes at one temperature, and their absorbances read after removal and quenching. This procedure was repeated at successively higher temperatures and plots made, of which Fig. 8 (lower half), for 1062 alone and with three levels of indole, is typical. The upper half of Fig. 8 shows for comparison dependence of deposit on concentration (from reference [9]).

Examination of this figure shows that breakpoints determined for a Δ(absorbance) of either 0.050 or 0.100 are practically unaffected by indole addition, in general agreement with Daniel's weight deposition data. Corresponding results for pyridine additions (Fig. 9) show that pyridine concentration has only a minor influence on breakpoint for Δ(absorbance) = 0.100 but somewhat more for Δ(absorbance) = 0.050. This slight effect with pyridine contrasts with the marked dependence of deposit weight on pyridine level.

In an extension of this contaminant work, Daniel looked at the effect on Jet A stability of a large number of nitrogen containing additives at one level, in an attempt to find chemical features (basicity, steric effects) that might account for the differences he observed in degradation rates.

We examined the effect of eleven of these reagents, at a concentration corresponding to 50 ppm nitrogen in each case, on the absorbance behaviour of 1062. Results are presented in Figs. 10-13, grouped by compound type, with the baseline fuel appearing for comparison in each. For nine of the eleven additives, the absorption at a concentration of 50 ppm nitrogen was negligible compared to that of the fuel itself, so that absorbance-time curves start from nearly the same point. The two exceptions were carbazole (Fig. 13) which at this concentration raises the initial absorbance by about 0.4 units; and 8-hydroxyquinoline whose absorbance (Fig. 10) was so great that it was necessary to use 0.1 cm path length cuvettes.

Daniel reported the relative degradative effect of these compounds, again in terms of deposit weight after 168h, as:

TABLE 2

EFFECT OF ADDITIVES ON RELATIVE DEPOSITION RATES FROM FUEL

ADDITIVE	DEPOSIT, $g/mm^2 \times 10^7$
Control (no additive)	3.4 ± 0.3
Pyridine	3.6 ± 0.3
2,6-lutidine	10.0 ± 1.4
2,4,6-trimethylpyridine	4.7 ± 0.2
Quinoline	7.7 ± 0.0
2,6-dimethylquinoline	8.2 ± 0.7
8-hydroxyquinoline	8.1 ± 0.2
N-methylpyrrole	8.7 ± 0.6
Pyrrole	3.5 ± 0.5
Indole	3.9 ± 0.3
2-methylindole	5.9 ± 0.3
Carbazole	2.6 ± 0.3

Comparison of this deposition data with the curves of Figs. 10-13 shows no correlation in either the short or long term. For example, toward the end of the runs of Fig. 10, the absorbance-time curve for the control, initially low, crossed and surpassed those of the three pyridine-based additives. The relative deposition rates reported by Daniel showed a quite different order, being for the control, pyridine, lutidine, and trimethylpyridine, 3.4, 3.6, 10.0 and 4.7. That the two processes, solids deposition and absorbance increase, operate independently is illustrated for all the materials in Fig. 14. Increase in absorbance over the unheated material after heating times of 7 and of 2 hours, is plotted against Daniel's deposit weights. The random scatter of results is further confirmation that there is no relation between these two aspects of fuel response to thermal stress.

It was observed that several of the treated fuels developed on heating a colour characteristic of the contaminant. Thus, indole and

pyrrole imparted a pale orange and a violet colour to the fuels they were added to. These same colours could be produced using, instead of the jet fuel, reagent decane, (itself quite resistant to prolonged heating at 150°C) and are almost certainly due to oxidation products of the additives themselves. The occurrence of coloured products is an interference not contemplated in the development of the Phillips test, and is discussed below.

3.3 Fuel Additives

The suspected interference of some additives in the Phillips breakpoint determination prompted a survey of these effects, primarily with the additive-free Jet A-1 1091. Three additives were employed.

a) ethylene glycol monomethyl ether (EGME), called for in a number of specifications, chiefly military, as a fuel system icing inhibitor (FSII). Eastman Kodak scintillation grade material, code 13072, was used.
b) Tolad 245*, an anti-corrosion agent of proprietary nature which also acts as a lubricity improver at high temperatures.
c) An antioxidant, 733 PDA 50**.

Results are presented below in summary form.

EGME - This material was introduced into two fuels, additive-free 1091 and 1062 containing the normal complement of additives but not fuel system icing inhibitor. The level used was 0.2% V/V slightly above the recommended maximum of 0.15% [10].

Figure 15 shows the general absorbance-time behaviour over several hours heating for the fuels with and without EGME. The effect is insignificant for 1062, but marked for 1091. Breakpoint determinations, which are influenced by initial behaviour, are summarized in Table 3, and these show a measurable decrease in stability for both fuels.

TABLE 3

EFFECT OF FUEL SYSTEM ICING INHIBITOR ON ABSORBANCE

	1091	1091 + EGME	1062	1062 + EGME
Δ(absorbance) 0.05	141	134	157.5	141
Δ(absorbance) 0.100	158	152	163	157

*provided through the courtesy of Tretolite Division, Petrolite Corporation of Canada.

**provided through the courtesy of Ethyl Canada. It consists of approximately 50% mixed tertiary phenols and 50% N,N'-di-sec-butyl-p-phenylenediamine.

Tolad 245 - was blended into fuel 1091 at a level of 45 mg/l, in the concentration range commonly employed. As Fig. 16 shows, there is no detectable effect on absorbance-time curves. Table 4, summarizing breakpoint determinations, shows a decline of 5-6°C for both absorbance increase levels.

TABLE 4

EFFECT OF TOLAD 245 ON ABSORBANCE

	1091	1091 + Tolad
Δ(absorbance)0.05	141	135
Δ(absorbance)0.100	156	151

733 PDA 50 - The effect of amine-type nitrogen-containing additives on Jet A-1 was invariably to accelerate the initial absorbance buildup on heating when compared to the control (see, e.g., Figs. 6 and 10). The active components of antioxidants are phenylenediamine derivatives and hindered phenols. These compounds are in general readily oxidized to highly absorbing substances, and while the exact mechanism of their protective action is not in question here, it is probably by the breaking of oxidative chain reactions, the antioxidant acting in a sacrificial role and producing coloured products. A number of experiments were conducted, employing additive-free Jet A-1 (1091) as received, and after treatment with antioxidant 733 PDA 50 at 5, 15 and 25 mg/litre. Figure 17 depicts 7 hour runs, using the fuel with no additive and with 25 mg/litre. An acceleration in absorbance buildup is seen, followed by a slower rise which at the highest antioxidant level nearly flattens out after several hours. Runs with fuels containing 5 and 15 mg/l antioxidant, not shown here, lay between the two curves of Fig. 17. On the other hand, breakpoint determinations on the same system (Table 5) show that by this criterion the stability is unaffected.

TABLE 5

EFFECT OF ANTIOXIDANT ON ABSORBANCE

	1091	1091 + 5 mg/l	1091 + 15 mg/l	1091 + 25 mg/l
Δ(absorbance)0.05	145	146	145.5	145
Δ(absorbance)0.100	153	154	151	152

Additive Effects - Summarizing the observations above,

a) EGME depresses breakpoints for both 1062 and 1091 fuels, but the effect on absorbance-time curves is fuel-dependent.
b) When fuel 1091 was treated with anti-oxidant 733 PDA 50, absorbance buildup was accelerated but breakpoints were unaffected.
c) Tolad 245 added to 1091 had just the reverse effect on these two properties to that of the antioxidant.

Thus there is no correspondence between changes in the earliest (30 min) stages of heating, and optical observations made over a period of some hours.

More generally, the Phillips method, with an absorbance measurement made at a single wave length, assumed that the only process contributing to absorbance change was micelle formation with a resultant non-specific increase in light scattering and diminished transmittance. The formation of absorbant substances calls this assumption in question, in particular antioxidants whose coloured products are in fact evidence of their protective action. The experiments described above, while by no means complete or systematic, suggest that general trends in absorbance with time and temperature, or the conceptually simpler breakpoint, are subject to interferences. These interferences obscure any correlations with thermal stability as measured by more objective methods based on solid deposition, the phenomenon of practical importance.

Copper - Smith [11] surveyed the effect of incubation with a variety of metals and alloys on the thermal stability of a specification jet fuel, employing the ASTM-CRC coker and the high temperature coker. He observed extreme sensitivity of the fuel to copper and its alloys. As a criterion of fuel susceptibility he determined changes in the fuel 'threshold' temperature, similar to the JFTOT breakpoint described above. With the fuels he employed, measurable deterioration was seen after relatively brief contact with copper, even at room temperature.

In a survey of copper effects, the metal was brought in contact with jet fuels at room temperature for varying periods of time, then removed, and absorbance changes followed during subsequent heat stressing. Copper foil was cleaned with dilute nitric acid, thoroughly rinsed and dried, and introduced to the fuel at a ratio of 80 cm^2 total surface per 100 ml fuel. In other experiments copper was introduced into solution as the fuel-soluble copper naphthenate*, and its effect compared with that of metallic copper.

Figure 18 shows that the effect of prior room temperature contact on the absorbance-time behaviour of 1062 fuel subjected to thermal stress is negligible, even after 29 days exposure. In the experiments summarized in Table 6 breakpoint determinations were shown to be quite unaffected by contact with copper.

---

*provided through the courtesy of Witco Chemicals Canada.

TABLE 6

EFFECTS OF METALLIC COPPER ON ABSORBANCE BREAKPOINT OF 1062

	1062	COPPER (2.5 DAYS EXPOSURE)
Δ(absorbance)0.050	157.5	157.5
Δ(absorbance)0.100	163	163

For a closer comparison with Smith's observations, JFTOT breakpoints were measured on 1062 as received and after 2.5 days exposure to copper. No deterioration was observed, the breakpoint temperature being in both cases in the range 290-300°C, within the accuracy of the method.

Copper introduced as soluble naphthenate has a very different effect. Figure 19 depicts absorbance-time curves for 1062 fuel heated at 140°C in the presence of four levels of soluble copper. The effect is discernible even at the lowest level, 50 ppb copper The relation between this type of measurement and breakpoint is not very straight forward; as is seen from Fig. 20, at the three lowest levels of copper the breakpoint is unaffected, but falls 50-60°C at 5 ppm copper. Again, for comparison, JFTOT measurements were made on these fuels. Complete JFTOT breakpoints were not determined, but runs were made at 260°C, the specification temperature. Maximum TDR readings varied with concentration:

Conc. Cu ppm	.05	.5	1	5
TDR max	0	0	17	42
	pass	pass	marginal failure	severe failure

When metallic copper was incubated with fuel 1091, the rate of absorbance change was greatly increased (Fig. 21) and the breakpoint from absorbance reduced as shown:

TABLE 7

EFFECTS OF METALLIC COPPER ON ABSORBANCE BREAKPOINT OF 1091

	1091	1091 + COPPER
Δ(absorbance)0.050	145	133
Δ(absorbance)0.100	153.3	141.4

The absence of metal deactivator, one of the constituents in the additive package, may have been responsible for this difference.

Fuel 1075 showed a third type of behaviour with metallic copper. Absorbance change and absorbance-based breakpoint were not affected, but the stability as determined by JFTOT was degraded. When run at 260°C the initial 1075 fuel had a visual code rating $> 2 < 3$ and a maximum TDR rating of 12, that is, a marginal pass. After 2.5 days contact with copper, the visual rating was 4, and the TDR reading 51, corresponding to a bad failure. Hence, with this marginal fuel, i.e. tested just at its breakpoint, contact with copper resulted in a precipitous loss of stability. Overall, the effects of contact with metallic copper were highly fuel-specific.

4.0 SUMMARY

In this note the effects of a number of fuel additives and contaminants were examined. Interferences were found, suggesting that absorbance methods would have only a limited application.

So far as a comparison of our results with Daniel's could be carried, there was no connection between optical phenomena and the appearance of solid deposits on prolonged heating at 120°C. A direct comparison of the same set of specification fuels by optical and JFTOT examination appeared the most useful remaining object of investigation, using the JFTOT as a reference. It would then be possible to see whether stability trends in these fuels as determined by one method were observed in the other. This work was carried out at the same time as that described here, and is reported in another note.

5.0 REFERENCES

[1] CRC literature survey on the thermal oxidation stability of jet fuels, CRC Report No. 509, April 1979.

[2] American Society for Testing and Materials. Annual Book of ASTM Standards, Part 25. D3241, "Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)".

[3] Reynolds, T.W. NASA TMX-3551, June 1977.

[4] Bagnetto, L., "Thermal Stability of Hydrocarbon Fuels", APL TDR 64-89, Sept. 1965, and references cited there.

[5] Proceedings of the 27th Meeting of Working Party 15, Air Standardization Coordinating Committee, May 1982. The presentation from Shell Thornton has the most recent reference to the use of this test method.

[6] Snitserov, Yu. V., Khim i Tekhnol. Topliv i Masel, Nov. 1961 (II), pg. 55-59. (Shell Research Ltd., Thornton, Translation No. 1060).

[7] Schirmer, R.M., "Morphology of Deposits in Aircraft and Engine Fuel System", Society of Automotive Engineers Preprint 700258, presented at National Air Transportation Meeting, New York, NY April 1970.

[8] Review of Literature on Storage and Thermal Stability of Jet Fuels, RTD-TDR-63-4270, January 1964.

[9] Worstell, J.H., and Daniel, S.R., Fuel 60 481-484 (1981).

[10] CGSB Specification 3-GP-526M.

[11] Smith, J.D., Aircraft Engineering 39 19-26 (1967).

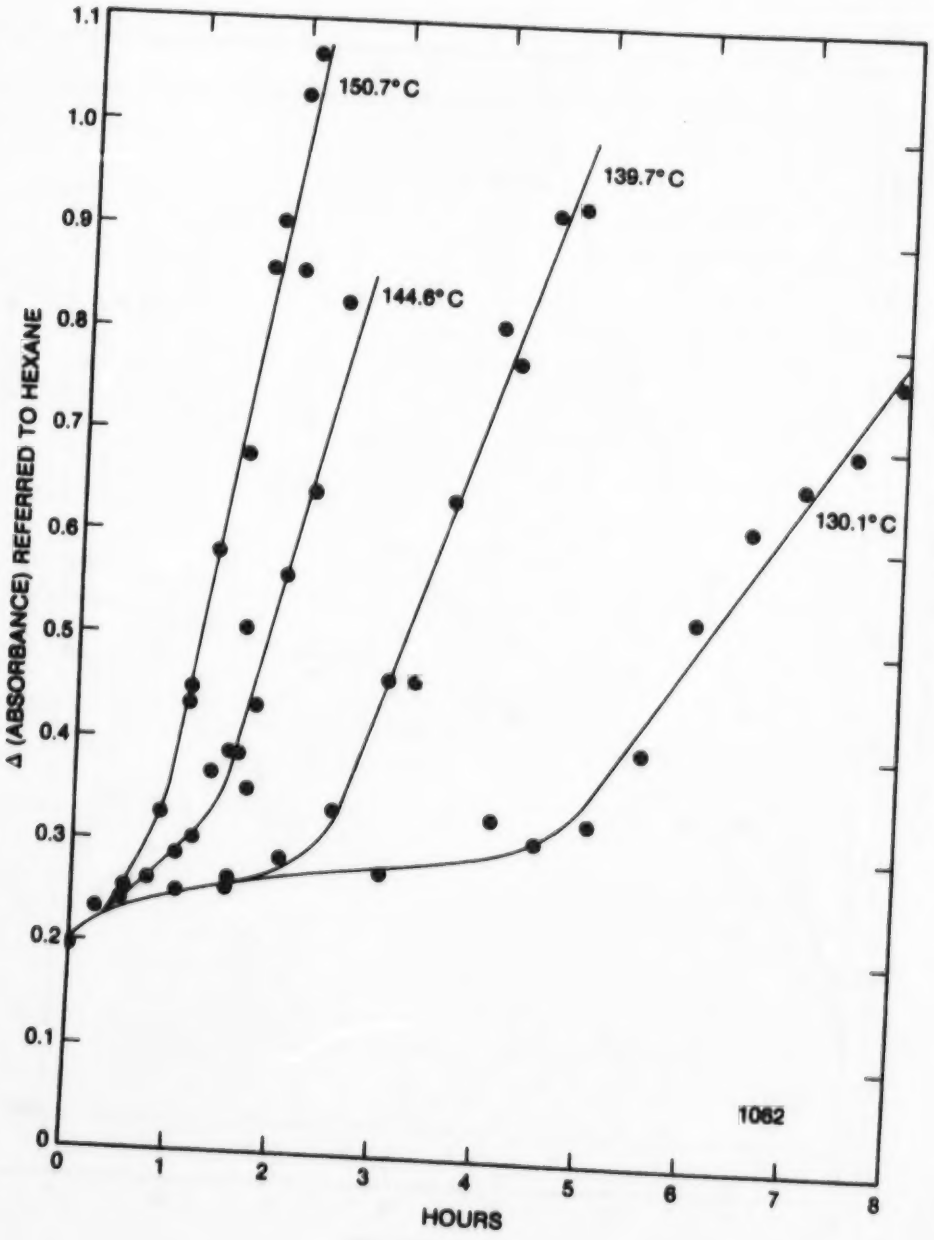

FIGURE 1 - Absorbance Change in 1062 Fuel as a Function of Time of Heating, at Several Temperatures

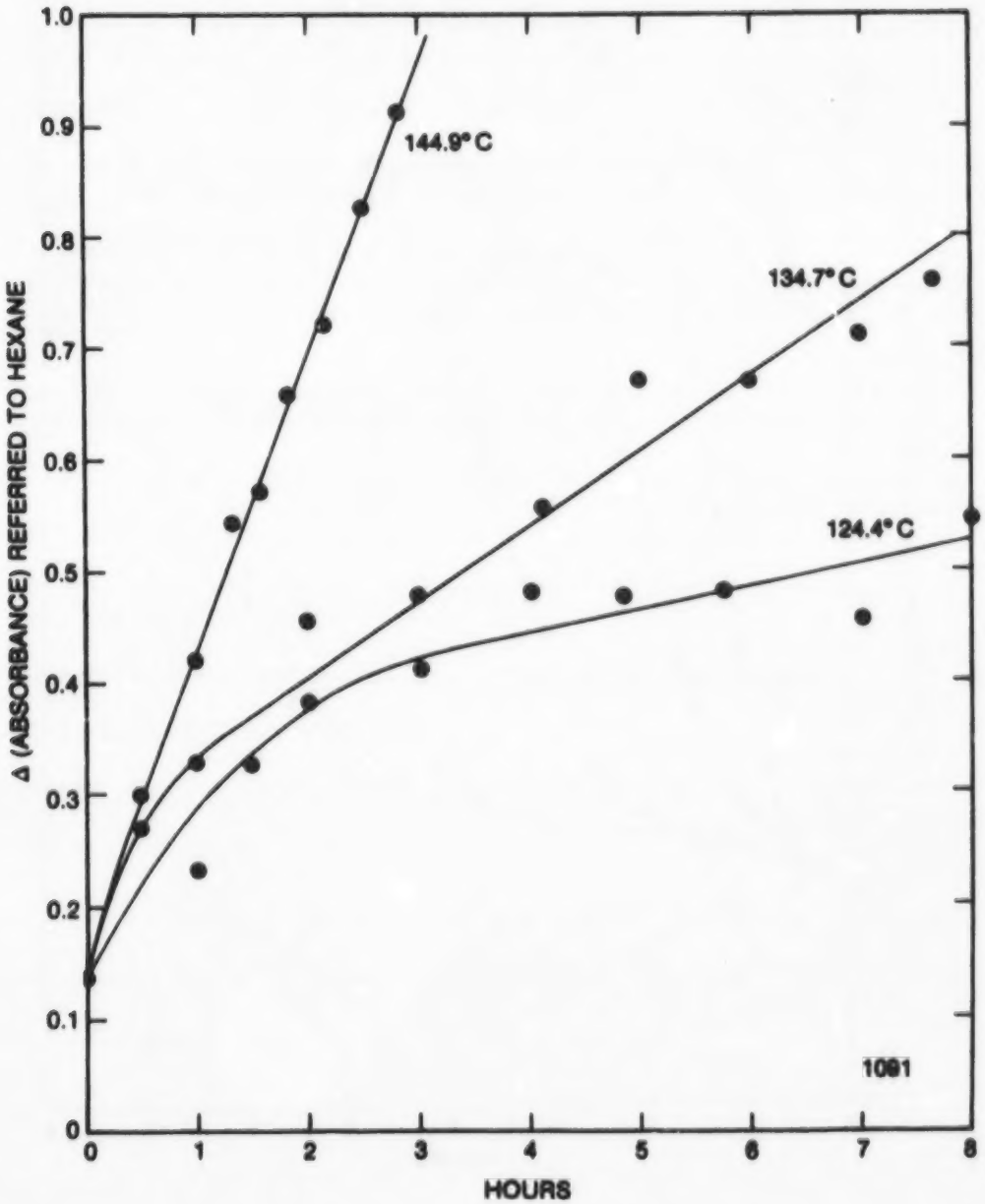

FIGURE 2 - As Figure 1, 1091 Fuel

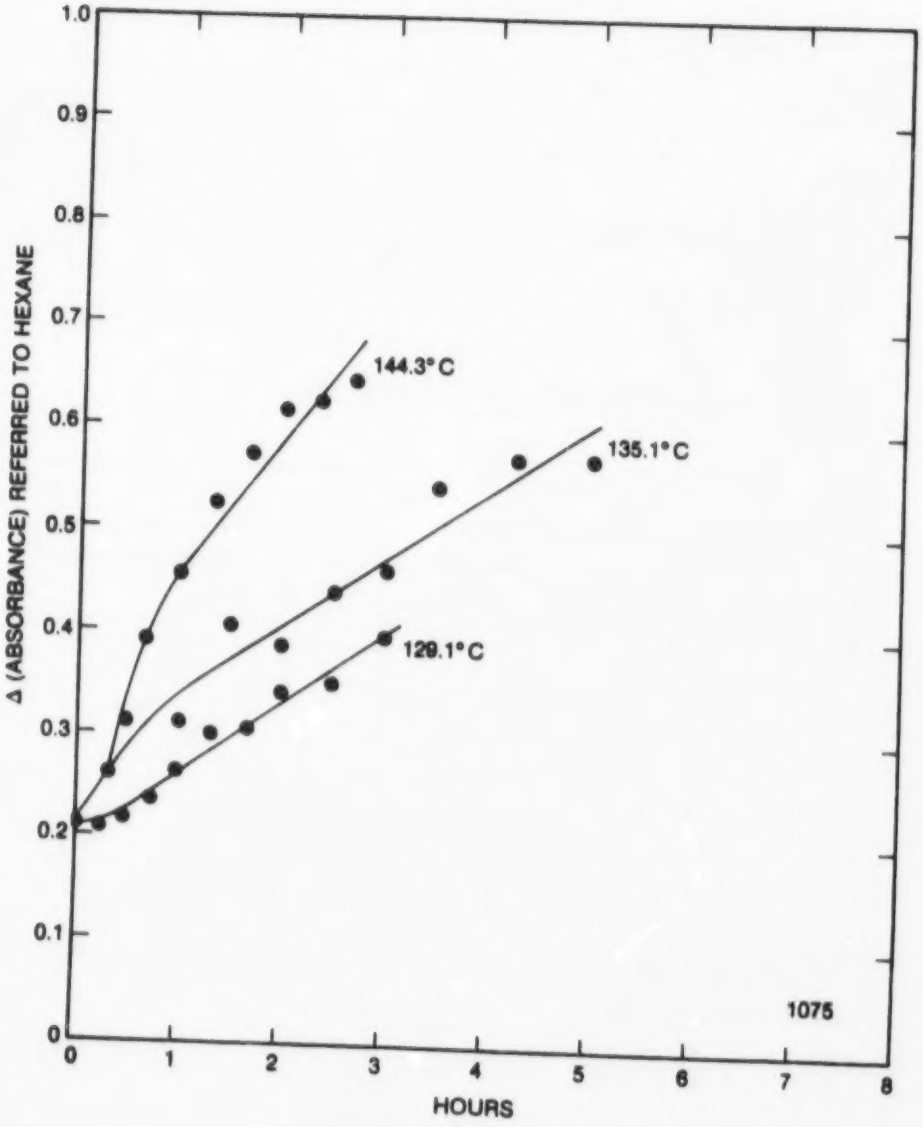

FIGURE 3 - As Figure 1, 1075 Fuel

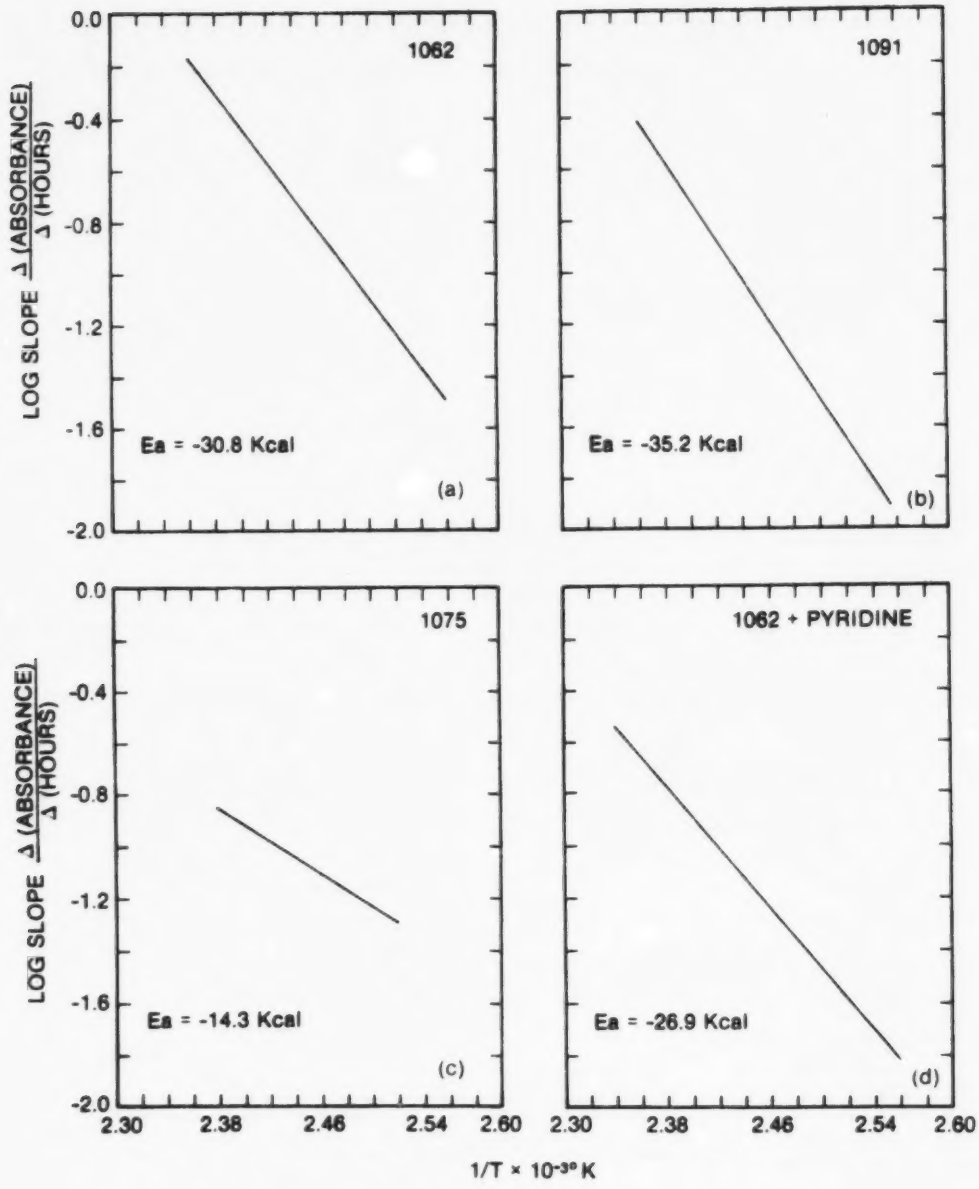

FIGURE 4 - Arrhenius Plots, Temperature Dependence of Rate of Absorbance Change (a) 1062 Fuel (b) 1091 Fuel (c) 1075 Fuel (d) 1062 Fuel + 50 ppm nitrogen as pyridine

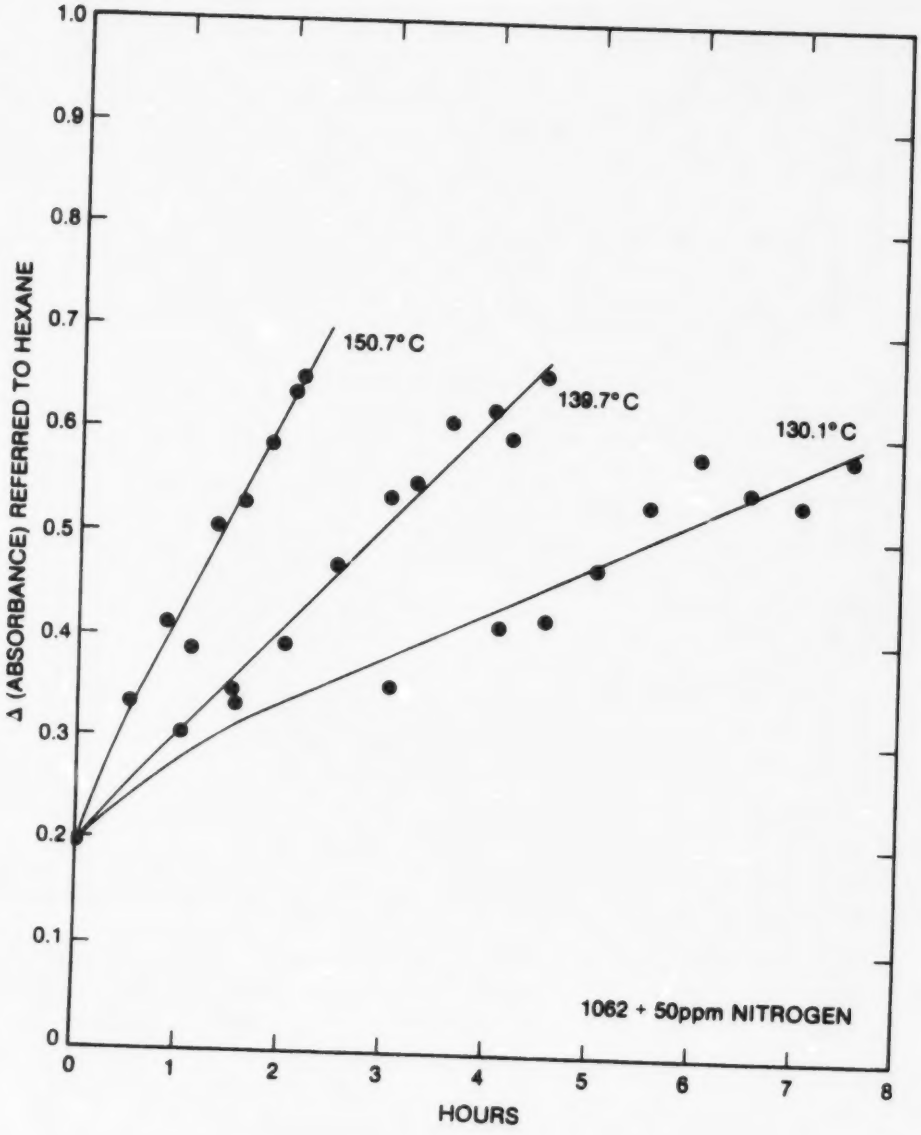

FIGURE 5 - As Figure 1, 1062 + 50 ppm Nitrogen as Pyridine

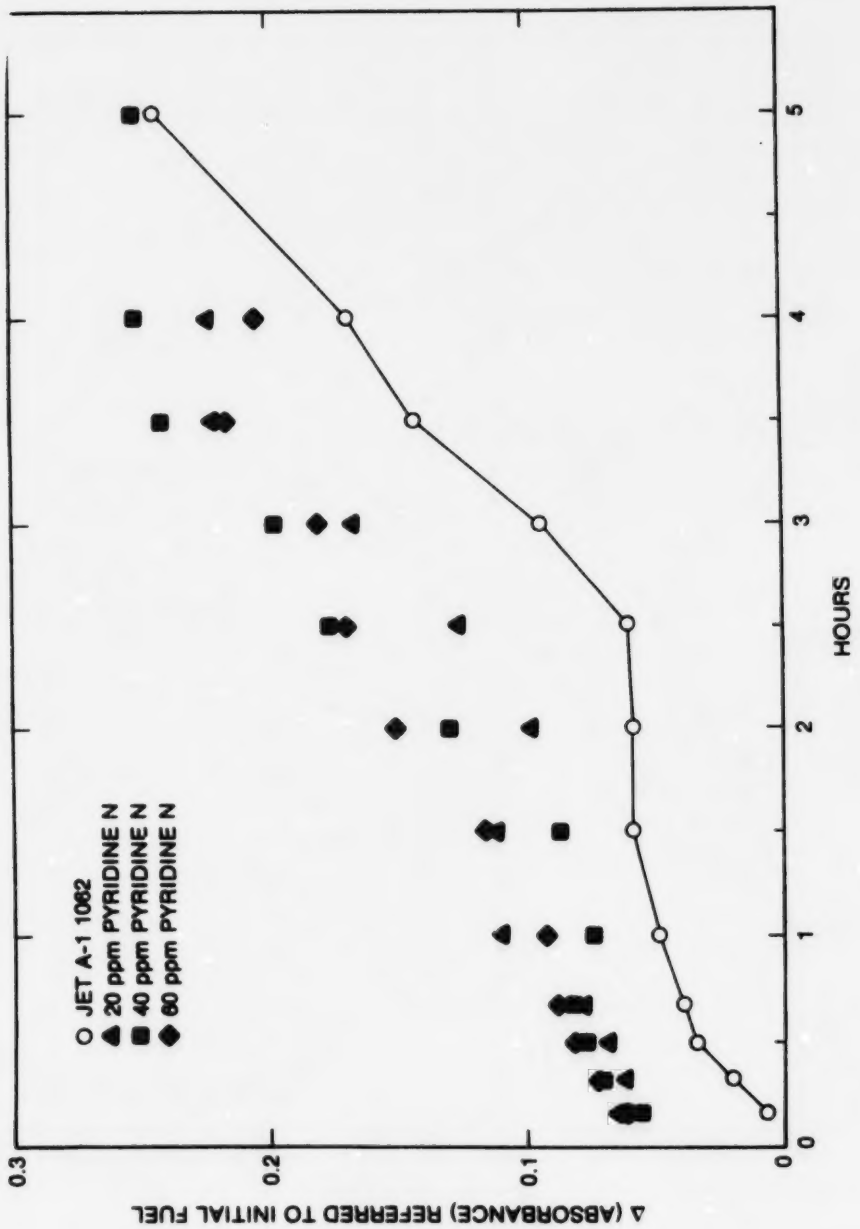

FIGURE 6 - Absorbance Change with Time for 1062 Fuel, Alone and with Three Levels Added Pyridine, 135°C

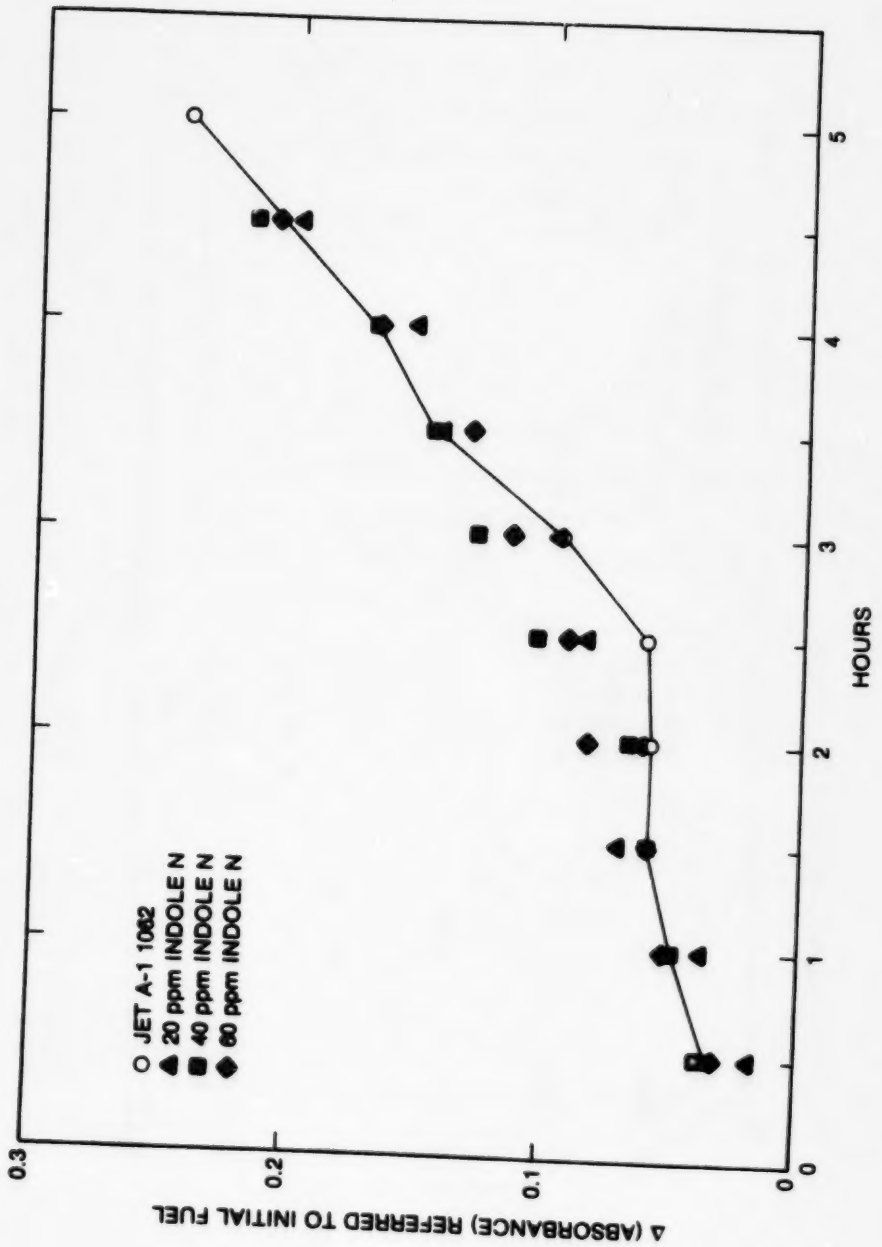

FIGURE 7 - As Figure 6, with Three Levels Added Indole

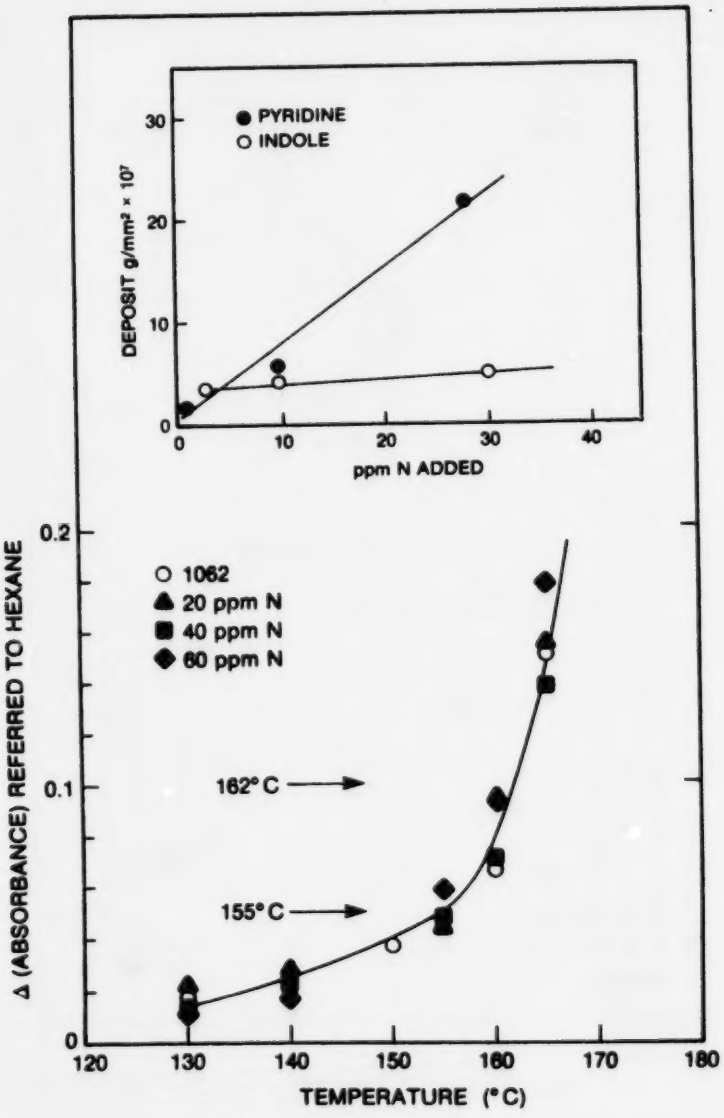

FIGURE 8 - (Lower) Breakpoint for 1062 Fuel, Alone and with Three Levels Added Indole (Upper) Deposition Effects in Jet A Fuel as a Function of Indole Concentration (from reference 9))

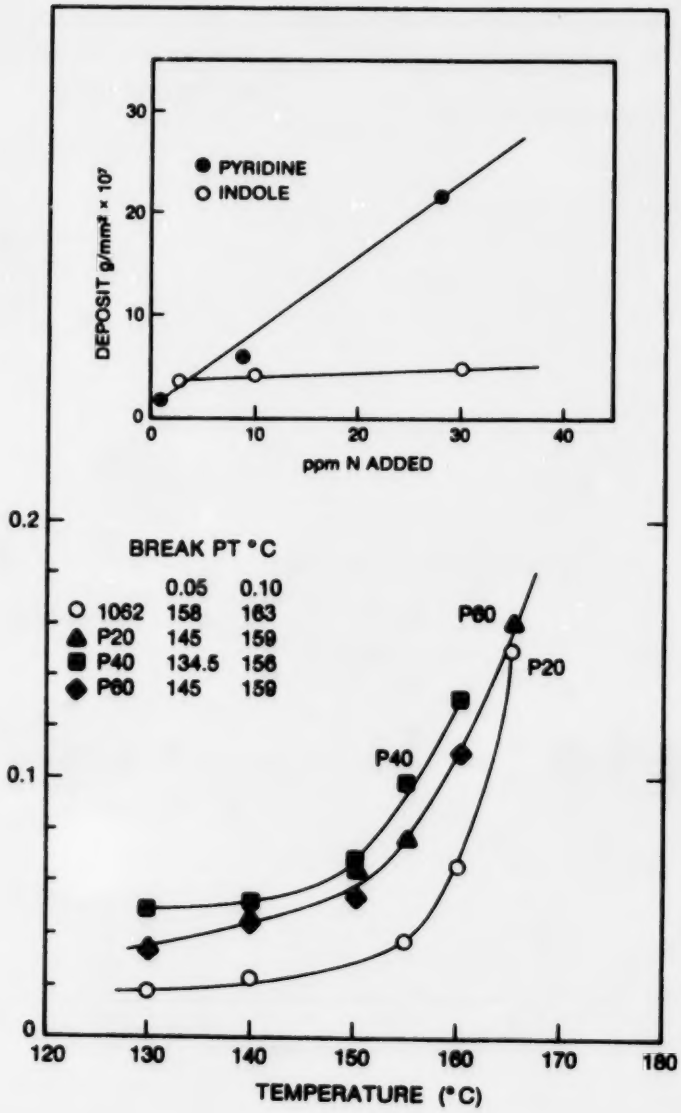

FIGURE 9 - As Figure 8, with Three Levels Added Pyridine

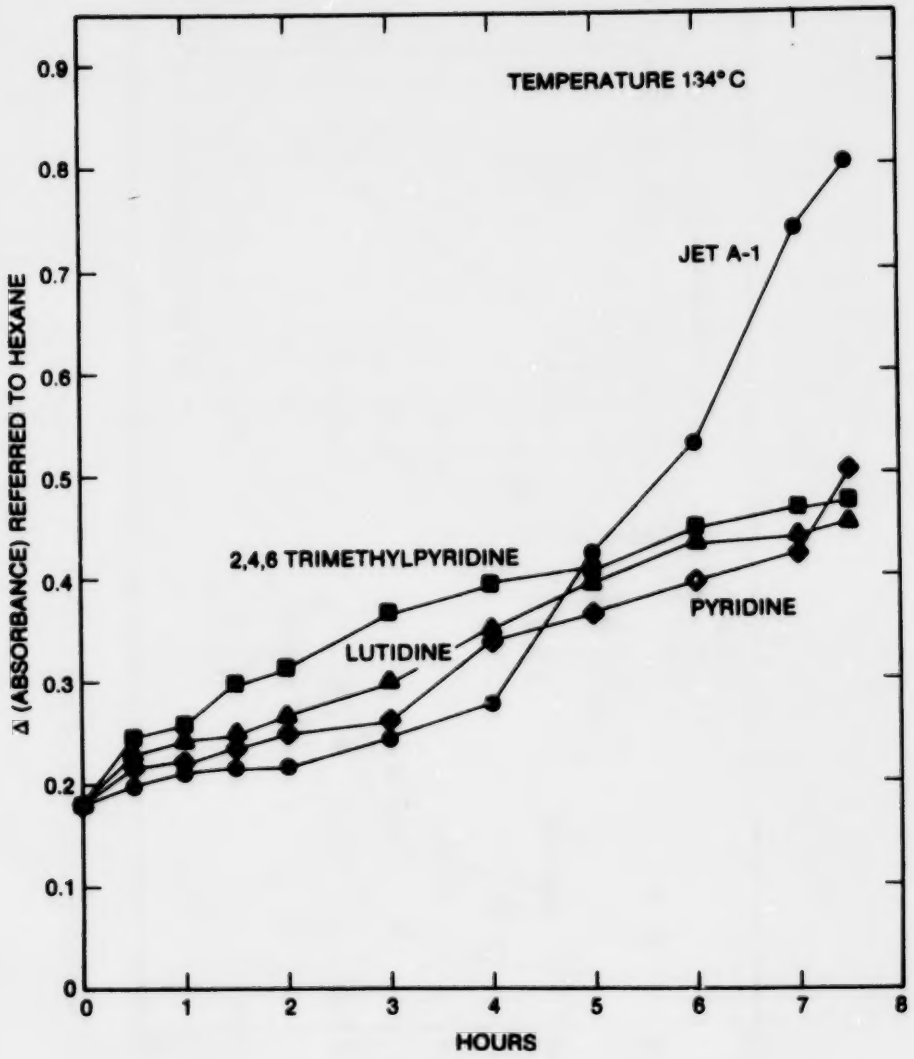

FIGURE 10 - Effect of Pyridine, 2, 6-Lutidine and Trimethylpyridine on Absorbance Change in Fuel 1062, 135°C

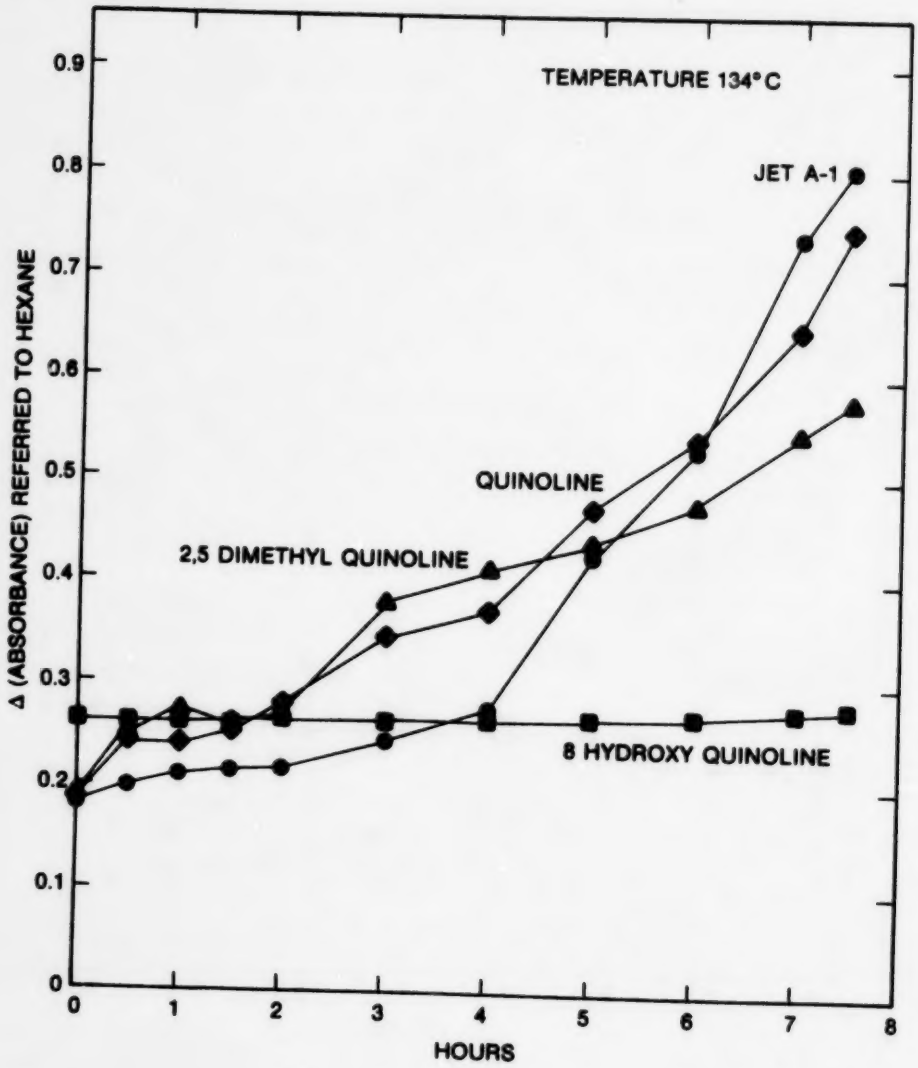

FIGURE 11 - As Figure 10, with Quinoline, 2, 5 Dimethylquinoline and 8-Hydroxyquinoline as Additives

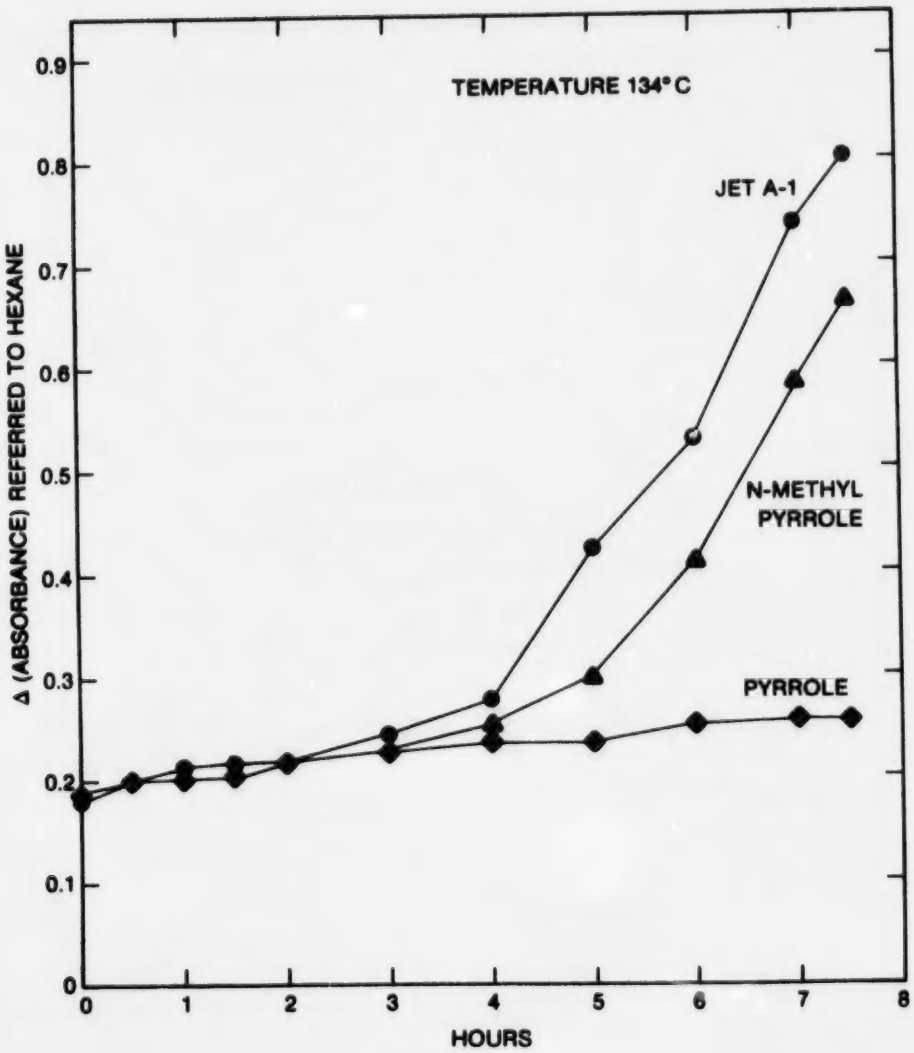

FIGURE 12 - As Figure 10, with Pyrrole, and N-Methylpyrrole as Additives

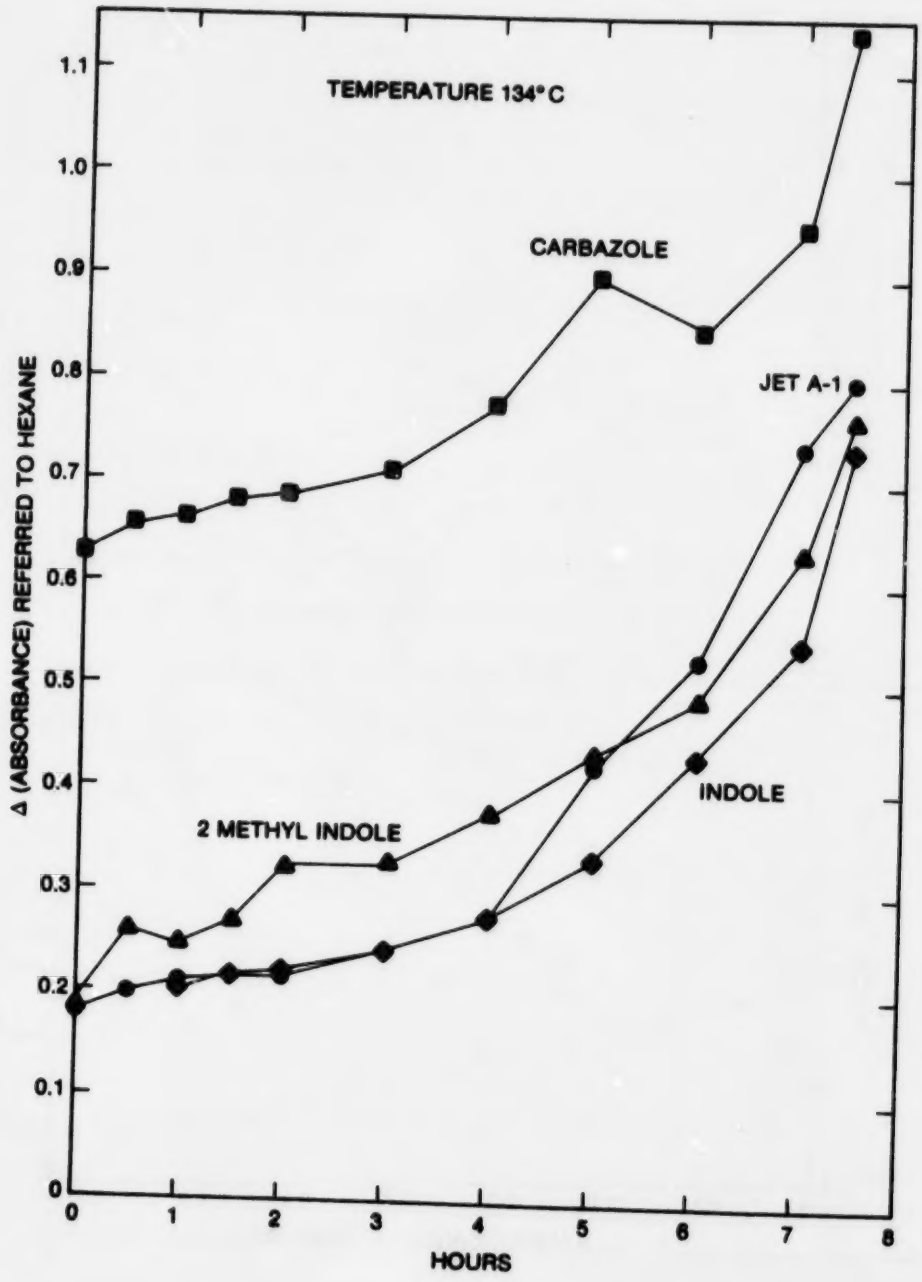

FIGURE 13 - As Figure 10, with Indole, 2-Methylindole and Carbazole as Additives

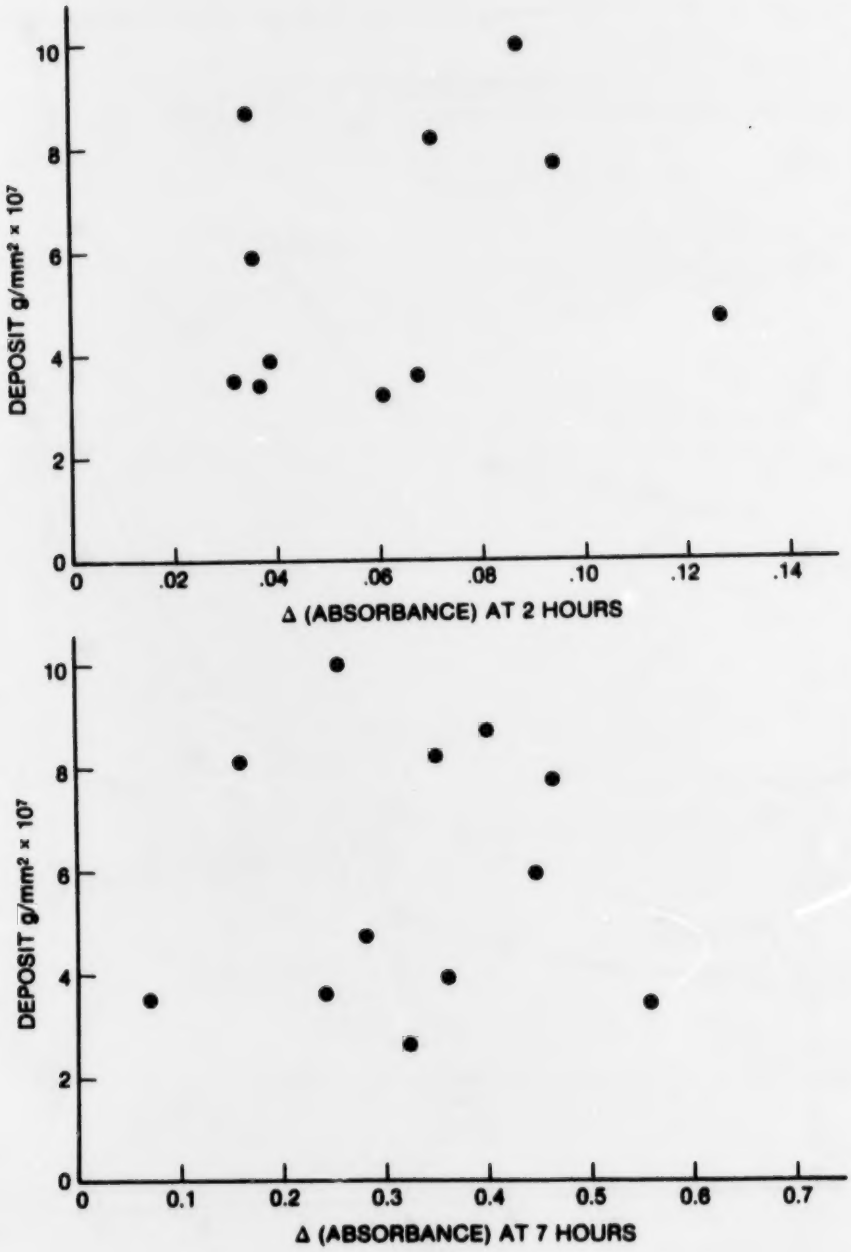

FIGURE 14 - Relation Between Effectiveness of Nitrogen Compounds in (a) Promoting Solids Deposition from heated Fuel (Ref. 9) and (b) Development of Absorbance in Heated Fuel

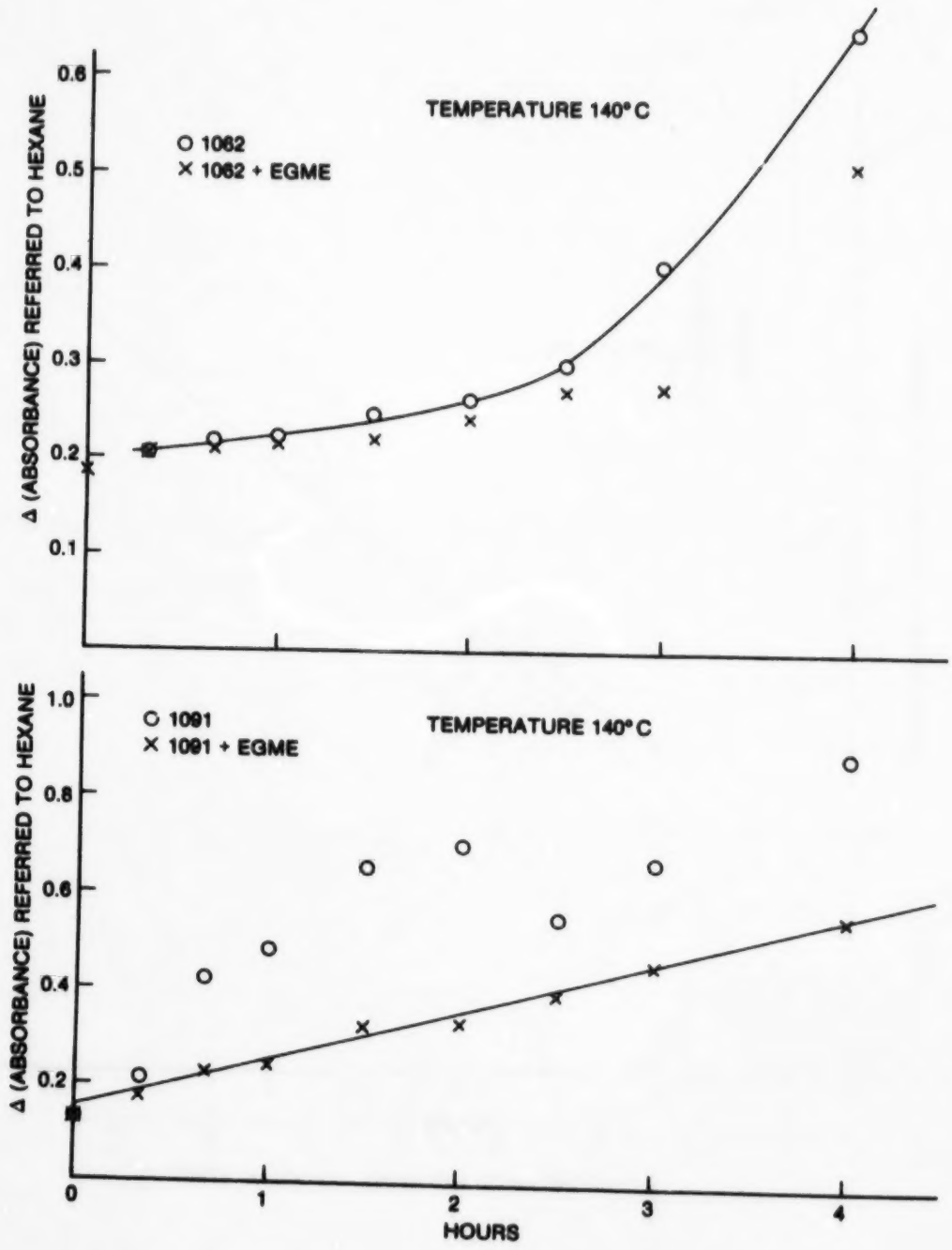

FIGURE 15 - Absorbance Change in Fuel 1091, Heated Alone and with EGME (0.2% V/V)

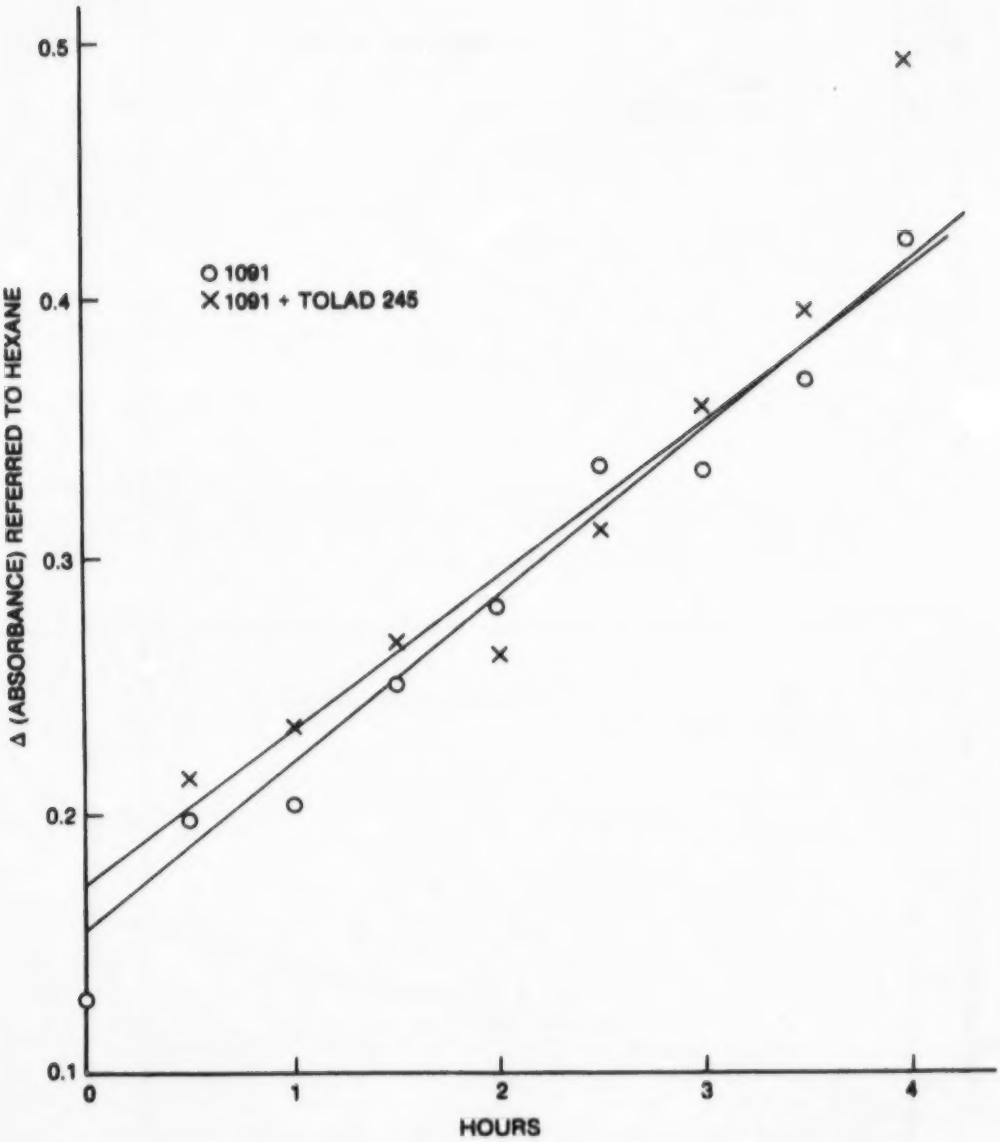

FIGURE 16 - Absorbance Change in Fuel 1091, Heated Alone and with Tolad 245 (45 mg/l)

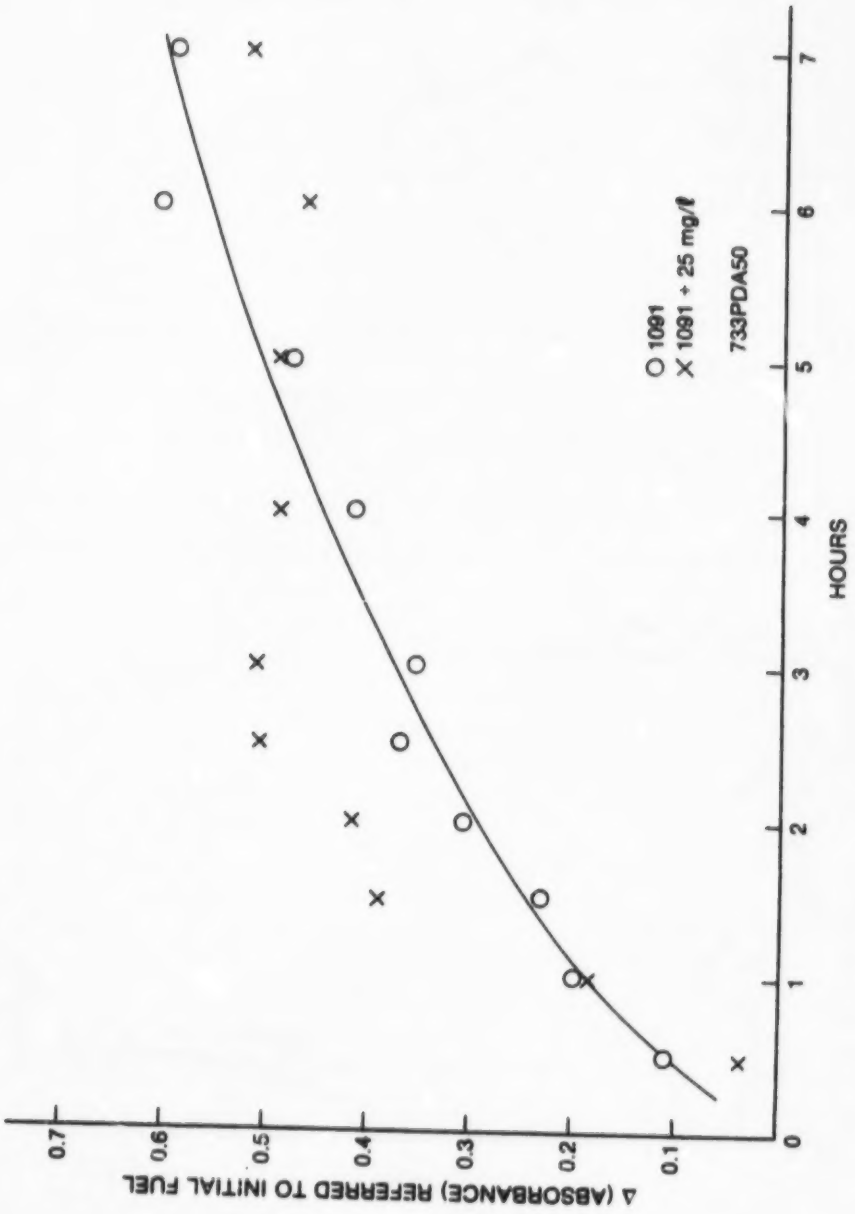

FIGURE 17 - Absorbance Change in Fuel 1091, Heated and Alone with Antioxidant 733 PDA 50 (25 mg/1)

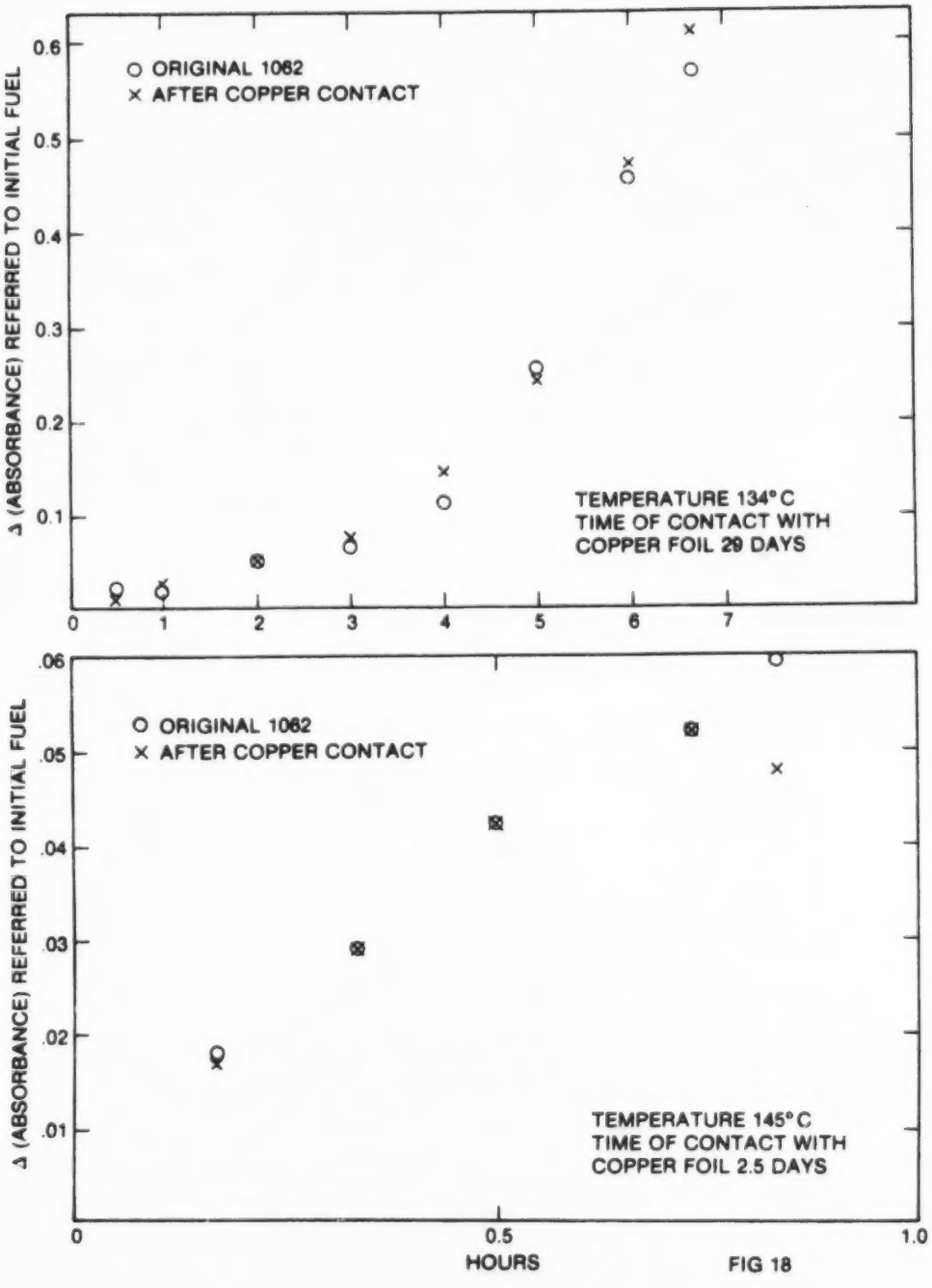

FIGURE 18 - Effect of Prior Room Temperature Contact with Metallic Copper on Absorbance Change in Fuel 1062, Conditions as Listed on Figure

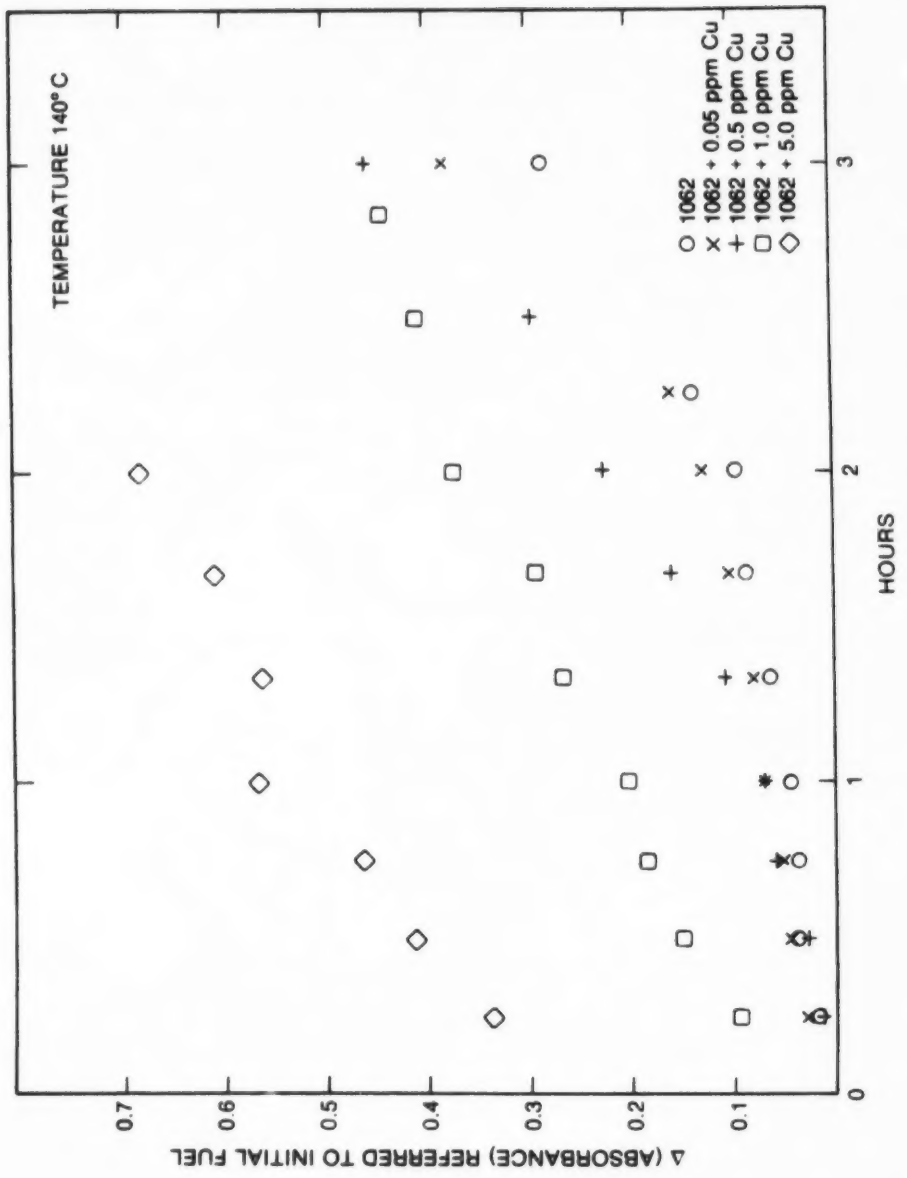

FIGURE 19 - Absorbance Change in Fuel 1062, Heated Alone and with Four Levels of Soluble Copper as Naphthenate

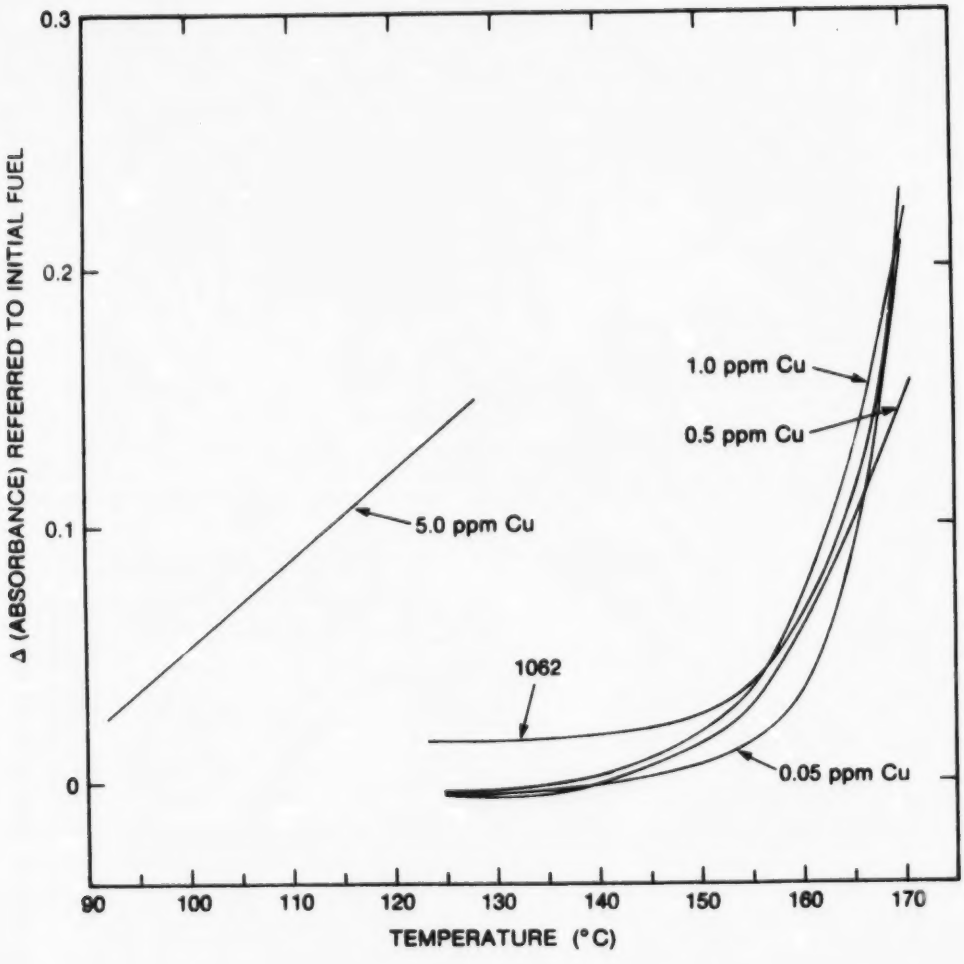

FIGURE 20 - Breakpoint of Fuel 1062, Alone and with Four Levels Soluble Copper as in Figure 19

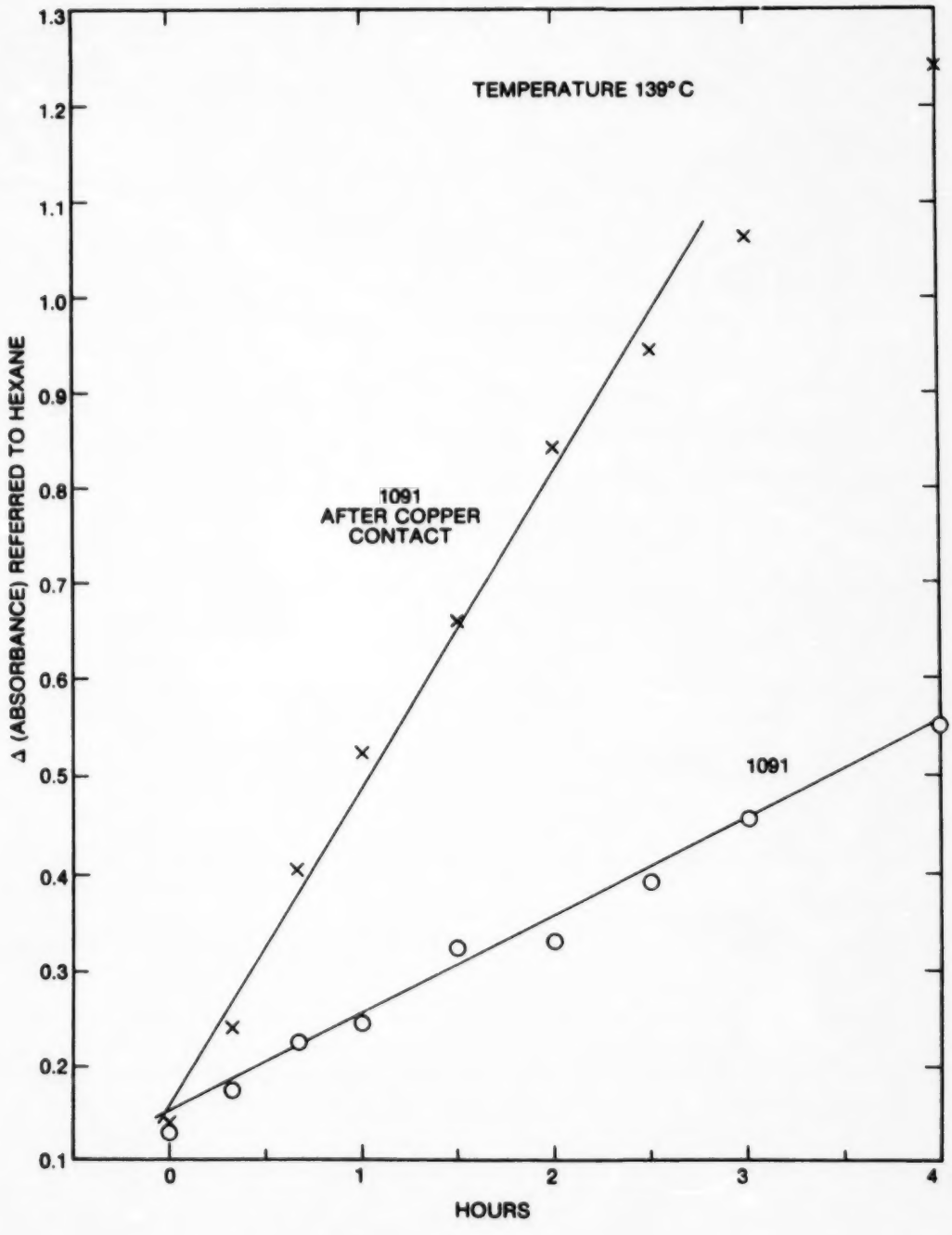

FIGURE 21 - Effect of Prior Contact (2.5 days) with Copper on Absorbance Change in Fuel 1091, Heated at 139°C

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY
Defence Research Establishment Ottawa
Ottawa, Ontario, CANADA, K1A 0Z4

2a. DOCUMENT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. DOCUMENT TITLE
ABSORBANCE CHANGES AS A MEASURE OF FUEL DEGRADATION

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Technical Note

5. AUTHOR(S) (Last name, first name, middle initial)
J.R. Coleman and L.D. Gallop

6. DOCUMENT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
DECEMBER 1983	33	11

8a. PROJECT OR GRANT NO.	9a. ORIGINATOR'S DOCUMENT NUMBER(S)
25B	DREO TN 83-33
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)

10. DISTRIBUTION STATEMENT
Unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY
	DREO

13. ABSTRACT

A method for following the course of thermal degradation of aviation turbine fuels was examined, based on the Phillips 5 ml bomb test, and measuring absorbance changes in the thermally stressed fuel at 340 mμ. Comparisons were made with a method based on direct measurement of weights of solid deposited from the fuel.

No correlation was found. The effects of a number of contaminants, and additives frequently employed in jet fuels was surveyed. No consistency was found, and it was concluded that the method offered little promise of being able to rate jet fuels in respect to their thermal stabilities.

DSIS
77-065

UNCLASSIFIED

Security Classification

KEY WORDS

Jet Fuel
Thermal Stability
Optical Absorbance
Antioxidant (733 PDA 50)
EGME
FS11
Anticorrosion Agent (TOLAD 245)

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the organization issuing the document.

2a. DOCUMENT SECURITY CLASSIFICATION: Enter the overall security classification of the document including special warning terms whenever applicable.

2b. GROUP: Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.

3. DOCUMENT TITLE: Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.

4. DESCRIPTIVE NOTES: Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.

6. DOCUMENT DATE: Enter the date (month, year) of Establishment approval for publication of the document.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the document.

8a. PROJECT OR GRANT NUMBER: If appropriate, enter the applicable research and development project or grant number under which the document was written.

8b. CONTRACT NUMBER: If appropriate, enter the applicable number under which the document was written.

9a. ORIGINATOR'S DOCUMENT NUMBER(S): Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.

9b. OTHER DOCUMENT NUMBER(S): If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).

10. DISTRIBUTION STATEMENT: Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this document from their defence documentation center."

(2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7½ inches long.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.